

## C L A I M S

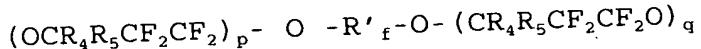
1. VDF polymerization process, optionally modified with small amounts, generally comprised between 0.1 and 10% by moles, of one or more fluoro-containing comonomers, carried out in the presence of a microemulsion comprising a (per)fluoropolyether having neutral end groups, or microemulsions of fluoropolyoxyalkylenes having hydrogen-containing end groups and/or hydrogen-containing repeating units, or microemulsions of fluoropolyoxyalkylenes having hydrogen-containing end groups and/or hydrogen-containing repeating units and hydrocarbons C<sub>1</sub>-C<sub>20</sub>, of aliphatic, aromatic or mixed type, optionally containing halogens, said fluoropolyethers having number average molecular weight from 400 to 3000, and a surfactant based on perfluoropolyethers with carboxylic end group salts, said surfactant having a number molecular weight Mn comprised between 400-600, preferably 400-550, and having a distribution of molecular weight such that fractions having a number average molecular weight higher than 700 are not present or are present in amount less than 5% by weight.
2. VDF polymerization process according to claim 1, wherein the surfactant based on perfluoropolyethers is a sodium

salt.

3. VDF polymerization process according to claims 1-2, wherein a microemulsion comprising a perfluoropolyether with neutral end groups is utilized.
4. VDF polymerization process according to claims 1-3, wherein chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP), tetrafluoroethylene (TFE) are utilized as comonomers.
5. VDF polymerization process according to claim 4, wherein the amount of modifying comonomer is comprised between 0.5-6% by moles.
6. VDF polymerization process according to claims 1-5, wherein the perfluoropolyethers with neutral end groups, optionally the end groups containing an hydrogen atom, utilized for preparing the microemulsions, comprise as repeating units sequences of one or more oxyfluoroalkylenic units such as  $-CF_2(CF_2)_zO-$ , wherein z is an integer equal to 1, 2 or 3,  $-CR_4R_5CF_2CF_2O-$  wherein R<sub>4</sub> and R<sub>5</sub> equal to or different from each other are chosen from H, Cl or perfluoroalkyl from 1 to 4 carbon atoms,  $-CF_2CF(CF_3)O-$ ,  $-CFYO-$ , wherein Y is equal to F or CF<sub>3</sub>.
7. VDF polymerization process according to claim 6, wherein the perfluoropolyethers have number average molecular weight comprised between 400 and 3000.

8. VDF polymerization process according to claims 6-7, wherein the perfluoropolyethers comprise as repeating units sequences of the classes:
- a)  $(C_3F_6O)_{m'}(CFYO)_{n'}$ , wherein the unit  $(C_3F_6O)$  and  $(CFYO)$  are perfluoroxyalkylenic units statistically distributed along the chain;  $m'$  and  $n'$  are integers such as to give the molecular weight indicated above, and  $m'/n'$  is comprised between 5 and 40, when  $n'$  is different from 0; Y is equal to F or  $CF_3$ ;  $n'$  can be also 0; said units inside the fluoropolyoxyalkylenic chain can optionally be bound among each other by a bond  $-O-R'_f-O-$ , wherein  $R'_f$  has the meaning defined in c);
  - b)  $(C_2F_4O)_{p'}(CFYO)_{q'}-(C_3F_6O)_{t'}$  wherein  $p'$  and  $q'$  are integers such that  $p'/q'$  ranges between 5 and 0.3, preferably 2.7-0.5, and such that the molecular weight is the one indicated above;  $t'$  being an integer with the meaning of  $m'$ , Y = F or  $CF_3$ ;  $t'$  can be 0 and  $q'/q'+p'+t'$  lower than or equal to 1/10 and the  $t'/p'$  ratio is from 0.2 to 6;
  - c)  $CR_4R_5CF_2CF_2O$  wherein  $R_4$  and  $R_5$  are equal to or different from each other and chosen from H, Cl or perfluoroalkyl, for instance having 1-4 C atoms, the

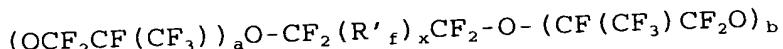
molecular weight being that indicated above, said units inside the fluoropolyoxyalkylenic chain being bound each other as follows:



wherein  $R'_f$  is a fluoroalkylenic group, for instance from 1 to 4 C, p and q are integers from 0 to 200, and p+q is at least 1 and such that the molecular weight is that indicated above,

d)  $CF(CF_3)CF_2O$

said units being linked each other inside the fluoropolyoxyalkylenic chain as follows:



wherein  $R'_f$  has the meaning indicated above, x is 0 or 1, a and b are integers and a+b is at least 1 and such that the molecular weight is that indicated above,

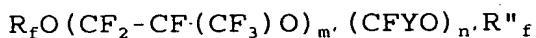
e)  $(C_2F_4O)_{a'}(CFYO)_{b'}$

wherein a' and b' are integers such that the molecular weight is inside the indicated range, a'/b' ranges between 5 and 0.3, preferably between 2.7-0.5, Y has the meaning indicated above.

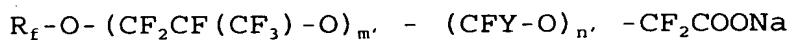
9. VDF polymerization process according to claims 1-8, wherein the neutral end groups of the perfluoropolyethers are perfluoroalkyls from 1 to 3 carbon atoms,

$\text{ClCF}_2\text{CF}(\text{CF}_3)-$ ,  $\text{CF}_3\text{CFClCF}_2-$ ,  $\text{ClCF}_2\text{CF}_2-$ ,  $\text{ClCF}_2-$ , in the case of microemulsions of fluoropolyoxyalkylenes having hydrogen-containing end groups, these are of the  $-\text{CF}_2\text{H}$ ,  $-\text{CF}_2\text{CF}_2\text{H}$ ,  $-\text{CFH-CF}_3$  type.

10. VDF polymerization process according to claims 1-9, wherein the perfluoropolyethers surfactants have the same repeating units indicated for perfluoropolymers.
11. VDF polymerization process according to claims 1-10, wherein the perfluoropolyethers have the following general formula:



having a random distribution of the perfluoroxyalkylenic units, whereien  $\text{R}_f$  and  $\text{R}''_f$  equal to or different from each other are neutral end groups as defined above,  $m'$  and  $n'$  are integers such as to meet the above requirements of molecular weight, Y has the meaning indicated above; the surfactant based on perfluoropolyether has the following formula:



wherein  $\text{R}_f$ ,  $m'$ ,  $n'$  and Y have the above meaning indicated.

12. VDF homopolymers or VDF copolymers modified with amounts comprised between 0.1-10% by moles of one or more fluorocarbonating comonomers according to claims 1-11.